

Comments to
Elaine by
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**REVISED DRAFT TECHNICAL MEMORANDUM NO. 4
SUMMARY OF PESTICIDE MONITORING
IN THE SACRAMENTO-SAN JOAQUIN DELTA WATERSHEDS
CALIFORNIA URBAN WATER AGENCIES
STUDY OF DRINKING WATER QUALITY IN DELTA TRIBUTARIES**

September 19, 1994

Pesticides were not included in the list of *contaminants* of concern to be evaluated in the Study of Drinking Water Quality in Delta Tributaries because previous reviews of pesticide data (*circa 1990*) indicated that most pesticides were not detected in the Sacramento and San Joaquin rivers and Delta waterways; and when pesticides were detected they were found at concentrations well below drinking water standards. *However, a number of pesticide studies have been conducted since 1990, making available additional information on a wider variety of pesticides and pesticide sources. These studies have largely focused on issues related to the effect of pesticides on fisheries and other aquatic biota. Because the health of aquatic resources has become the largest factor in water management of the Delta tributaries and because of the more recent information (at lower detection limits) available on more types of pesticides,* the Project Advisory Committee (PAC) determined that pesticide monitoring programs should be evaluated and the importance of pesticides as drinking water contaminants *in Delta tributary source waters* should be reassessed.

The purpose of this technical memorandum is to summarize the information and results of pesticide monitoring programs conducted by various agencies in the Delta watersheds and to relate that information to this study. The relationship to this study involves the impact of pesticides on drinking water quality, the advisability of including pesticides in the loads calculations for this study, and assessing the need for additional pesticide monitoring with respect to drinking water quality effects.

It should be clearly stated that the monitoring programs and data discussed herein refer to sources of drinking water, not to drinking water itself. Between the source and the drinking water delivered to consumers is the water treatment plant, designed to remove contaminants of

concern to human health and aesthetic considerations (such as taste and odor) from the source water. Understanding the quality of the source water is nevertheless of concern to water utilities.

The discussion of recent pesticide monitoring is prefaced with a summary of pesticide issues as discussed in the State Water Project (SWP) Sanitary Survey Report (Brown and Caldwell, 1990). The information on pesticide monitoring programs is then organized as follows:

1. Delta monitoring programs.
2. Delta tributary monitoring programs.
3. *Pesticide issues regarding water treatment plant operations.*

The final section of the memorandum contains *findings* and recommendations with regard to this study.

SUMMARY OF PESTICIDE ISSUES AS DISCUSSED IN THE 1990 SWP SANITARY SURVEY REPORT

Pesticides were discussed in the SWP Sanitary Survey (Brown and Caldwell, 1990) relative to one type of contaminant source, namely agricultural drainage. Agricultural drainage was discussed in that report for three geographic areas: the Sacramento River watershed, the San Joaquin River watershed, and the Delta. Agricultural drainage was discussed in terms of nutrients, metals, and other constituents as well as pesticides. Monitoring information included in that report generally consisted of data through 1988-1989. The pesticides monitoring information summarized in that report is discussed in more detail later in this memorandum.

The pesticides discussed in the Sacramento River watershed were primarily the two rice herbicides molinate (Ordram) and thiobencarb (Bolero). *These herbicides were of concern due to taste and odor problems with Sacramento River water rather than due to human health issues.* These pesticides are carried from the rice fields through the river system primarily in May and

June of each year. The SWP Sanitary Survey examined the decline in the concentrations of these pesticides in the Sacramento River since the early 1980s. This decline was a result of agricultural management practices, introduced by the Department of Pesticide Regulation (DPR) *and cooperated with extensively by rice growers*. These management practices primarily consist of holding the treated water for longer periods before discharge. Longer holding times allow these pesticides to degrade and dissipate. *The decline in rice pesticides in the Sacramento River has been dramatic over the past 10 years. Table 1 below shows the reduction in molinate and thiobencarb loads.*

By 1990, some *aquatic* toxicity testing in rice field drains conducted by the Central Valley Regional Water Quality Control Board (Regional Board) had identified the presence of other pesticides as a concern to aquatic life. *It should be noted that where toxicity is discussed in this technical memorandum, it refers to aquatic toxicity rather than toxic effects to humans. Moreover, it should be noted that tests for aquatic toxicity are made in the laboratory under necessarily artificial conditions with test species not necessarily resident to the stream from which the water being tested was collected. These tests, therefore, indicate rather than conclusively prove occurrence of toxicity to aquatic organisms in the stream itself.*

Since 1990, several developments concerning rice field pesticides have occurred. The Regional Board has instituted performance goals for five pesticides in agricultural drainage (*four of which are used in rice fields*). The concentrations of molinate and thiobencarb have ceased their rapid decline and *currently appear to fluctuate about* their respective performance goals. Additional studies have been conducted on the *aquatic* toxicity and pesticide concentrations of rice field drainage. Additional management practices have been studied and adopted. A more detailed discussion of these developments is provided in the section on Delta Tributary Monitoring Programs.

Two separate areas of the San Joaquin River watershed were discussed in the SWP Sanitary Survey: the subsurface agricultural drainage area on the west side of the watershed and the surface water agricultural drainage area on the east side. The primary concern with agricultural drainage on the west side of the San Joaquin River is salts and trace elements.

Table 1. Estimated Mass Transport of Molinate and Thiobencarb in the Sacramento River Past Sacramento in the Years 1982-1993

Year	Molinate, kg (pounds) transported		Thiobencarb, kg (pounds) transported	
1982	18,464.9	(40,666.9)	-- ¹	--
1983	2,752.9	(6,056.5)	623.7	(1,372.2)
1984	7,352.0	(16,174.4)	715.2	(1,573.5)
1985	6,014.8	(13,232.5)	2,317.5	(5,098.6)
1986	4,622.1	(10,168.7)	845.7	(1,860.6)
1987	2,342.3	(5,153.2)	22.8	(50.2)
1988	3,194.2	(7,027.2)	68.1	(149.8)
1989	1,984.1	(4,365.1)	11.4	(25.1)
1990	3,204.1	(7,049.1)	51.4	(113.1)
1991	99.2	(217.9)	0	(0) ³
1992	56.6	(124.7)	0	(0)
1993	2,006.9	(4,232.4)	0	(0)

¹Mass transport was not calculated due to incomplete monitoring data.

²The Colusa Basin Drain, a major agricultural drainage canal, did not contribute to the mass transport at Sacramento during all or part of the sampling period because the drain was routed into the Yolo Bypass during unusually high Sacramento River flows.

³Thiobencarb was not detected in the Sacramento River in 1991-1993 (limit of detection = 0.1 parts per billion).

Note: Table is cited from Department of Pesticide Regulation. March 1994. Information on Rice Pesticides Submitted to the Central Valley Regional Water Quality Control Board.

Limited pesticide monitoring had been conducted on that drainage. On the east side, some *aquatic* toxicity testing conducted by the Regional Board had identified the presence of *aquatic* toxicity in the San Joaquin River attributed primarily to the surface agricultural drainage.

Since 1990, there has been *some* additional work on pesticides in the subsurface drainage conducted as part of the San Joaquin River Study. There has been considerable work conducted on the *aquatic* toxicity and pesticide chemistry of the surface agricultural drainage (*particularly from orchards*) in various studies. This work has recently expanded in geographic area and is now also being conducted in the Sacramento River watershed and in the Delta. This work is discussed in the section on Delta Tributary Monitoring Programs.

Delta islands agricultural drainage was discussed in the SWP Sanitary Survey Report principally with respect to trihalomethane formation potential (THMFP) and soils high in carbon content. The Interagency Delta Health Aspects Monitoring Program (IDHAMP) and the 1988 Delta Islands Drainage Investigation (DIDI) monitoring, conducted by the Department of Water Resources (DWR), had found a few pesticides at levels below drinking water standards. This work is discussed in the section on Delta Monitoring Programs.

In 1990, DWR combined the IDHAMP and DIDI into one monitoring program, the Municipal Water Quality Investigation (MWQI) Program. The primary focus of MWQI has been *the mineral quality of Delta waters, THMFP, and total formation potential carbon (TFPC), which is of broader significance in terms of organic disinfection by-products*. No further pesticide monitoring has been conducted under MWQI.

PESTICIDE STUDIES AND MONITORING PROGRAMS

Since the SWP Sanitary Survey Report was prepared, a number of studies and pesticide monitoring programs have been conducted. The recent studies and the studies discussed in the SWP Sanitary Survey Report are described in this section. Table 2 is a summary of monitoring

Table 2. Summary of Pesticide Monitoring Data in the Delta and Delta Tributary Watersheds

Pesticide issue/project	Agencies	Monitoring period	Major rivers monitored	Pesticides detected	Minor creeks, minor sloughs, drains monitored	Pesticides detected
IDHAMP	DWR	1983-1987	Delta	2,4-D, 4,4-DDD, 4,4-DDE, bentazon, BHC-alpha, BHC-beta, BHC-gamma, carbofuran, diazinon, dieldrin, dimethoate, endosulfan, guthion, methyl parathion, molinate, paraquat, parathion, simazine, thiobencarb	Delta drains	2,4-D, atrazine, bentazon, BHC-gamma, dacthal, glyphosate, molinate, thiobencarb
DIDI	DWR	1988	--	--	Delta drains	atrazine, bentazon, carbaryl, methamidophos, molinate, simazine
D-1485	DWR	1975-present	Delta	diuron	--	diuron
Water Hyacinth Control Program	DBW	1980-present	Delta; San Joaquin, Merced, and Tuolumne rivers	2,4-D	Salt Slough	2,4-D
National Stream Quality Accounting Network	USGS	1985, 1988	San Joaquin River at Vernalis	cyanazine, DDE, DDT, diazinon, dieldrin, ethion, lindane, metachlor, methyl parathion, parathion	--	--
San Joaquin River Bioassay Study	RWQCB	1988-1990	San Joaquin River	carbaryl, carbofuran, diazinon, dimethoate, methyl parathion	--	--
San Francisco Estuary Toxic Contaminants Program	USGS	1990-present	Sacramento River, San Joaquin River	carbaryl, carbofuran, chlorpyrifos, diazinon, methidathion, molinate, simazine, thiobencarb	--	--
San Joaquin River Study	DPR	1991-1993	San Joaquin, Merced, Tuolumne, and Stanislaus rivers	aldicarb, azinphos-methyl, carbaryl, carbofuran, chlorpyrifos, diazinon, dimethoate, endosulfan, malathion, methidathion, methiocarb, methomyl, oxamyl, parathion	Various drains and creeks	aldicarb, azinphos-methyl, carbaryl, carbofuran, chlorpyrifos, diazinon, dimethoate, endosulfan, fonofos, methidathion, methomyl, oxamyl, parathion, phosmet
Winter Wheat Study	DPR	1992	Feather River, Sacramento River	2,4-D, dicamba, MCPA	Colusa Basin Drain, Sutter Bypass	2,4-D, dicamba, MCPA

Table 2. Summary of Pesticide Monitoring Data in the Delta and Delta Tributary Watersheds (continued)

Pesticide issue/project	Agencies	Monitoring period	Major rivers monitored	Pesticides detected	Minor creeks, minor sloughs, drains monitored	Pesticides detected
Orchard and Alfalfa Study	RWQCB	1992	Sacramento, Feather, Mokelumne, San Joaquin, and Old rivers	bromacil, <i>diazinon</i> , diuron, flumeturon, methidathion, protham	Seven small Delta water-courses and six Delta sloughs	<i>carbofuran</i> , chlorpyrifos, <i>diazinon</i> , diuron
National Water Quality Assessment Program	USGS	1992-1994	San Joaquin River	chlorpyrifos, <i>diazinon</i> , metachlor, methidathion, <i>simazine</i> , triazine	--	--
Pesticide Tracer Study	USGS	1993	Sacramento and San Joaquin rivers, Carquinez Straights	<i>carbaryl</i> , chlorpyrifos, <i>diazinon</i> , methidathion	--	--
Rice Pesticide Control Program	DFG RWQCB DPR	1980-present	Sacramento River	<i>carbofuran</i> , <i>molinate</i> , <i>thiobencarb</i>	Major rice drains	bensulfuron methyl, <i>carbaryl</i> , <i>carbofuran</i> , chlorpyrifos, <i>malathion</i> , <i>methyl parathion</i> , <i>molinate</i> , <i>propanil</i> , <i>thiobencarb</i>
Rice Pesticides Transport Study	USGS	1990	Sacramento River	<i>carbofuran</i> , <i>molinate</i> , <i>thiobencarb</i>	--	--
Urban Runoff Toxicity Identification Evaluation Study	RWQCB	1993-present	--	--	Sacramento and Stockton urban creeks and drains	<i>diazinon</i>

Key to agency and project acronyms:

IDHAMP Interagency Delta Health Aspects Monitoring Program
 DWR Department of Water Resources
 DIDI Delta Islands Drainage Investigation
 DBW Department of Boating and Waterways
 USGS United States Geological Survey
 DFG Department of Fish and Game
 RWQCB Regional Water Quality Control Board, Central Valley Region
 DPR Department of Pesticide Regulation

Note: Pesticides with drinking water standards are *italicized*.

programs which have either focused on or included pesticide monitoring. This table shows the pesticide issue being studied, the agencies involved, the water bodies monitored, and the pesticides detected. Pesticides with drinking water standards are italicized. Table 3 shows drinking water standards *and criteria* for those pesticides, which have been detected in the Delta and Delta tributaries.

It should be noted that different monitoring programs at different times have used different field collection and laboratory analytical methods and have achieved different detection limits. In general, over time, sample collection procedures have become cleaner, laboratory analytical methods have become more accurate and precise, and detection limits have been lowered. These issues are noted here and it is also noted that this technical memorandum does not explore these issues in detail with respect to the data presented.

Delta Monitoring Programs

Two studies conducted specifically with regard to the drinking water quality of the Delta *source waters* have been conducted by DWR which included pesticide monitoring. These studies are the IDHAMP and the DIDI study. The monitoring programs conducted by DWR pursuant to D-1485 and the California Department of Boating and Waterways (DBW) are also discussed.

IDHAMP. DWR conducted this monitoring study primarily to characterize THMFP and general mineral water quality. The characterization of pesticide occurrence in Delta agricultural drains, the Delta channel system, and the headworks of the Delta export facilities was a relatively minor portion of the overall study.

The monitoring plan for pesticides was based on an evaluation of pesticide use in different counties; time of application; chemical water solubility, half-life, and partition coefficients; and the difficulty in treating with conventional water treatment processes. This evaluation was the basis for determining what pesticides would be most likely found in particular months and regions. The study was conducted from 1983 to 1987 during spring herbicide applications,

**Table 3. Drinking Water Standards and Criteria for Pesticides
Detected in the Delta and Delta Tributaries**

Pesticides, µg/l	Standard ^a	Highest concentration detected in major rivers ^b	Highest concentration detected in minor creeks, sloughs, drains ^b
2,4-D	70 ^c /100 ^d	~10	~10
Atrazine	3 ^d	--	0.91
Bentazon	18 ^d	~2.8	~2.8
Carbaryl	60 ^e	3.95	8.4
Carbofuran	18 ^d	1.33	4.4
Cyanazine	1 ^f	0.10	--
Diazinon	14 ^e	1.53	36.8
Dicamba	200 ^f	-- ^g	-- ^g
Dieldrin	0.05 ^e	0.005	--
Dimethoate	140 ^e	2.44	2.23
Ethion	35 ^e	0.01	--
Glyphosate	700 ^d	00	10.0
Lindane	0.2 ^e /0.04 ^h	0.002	--
Malathion	160 ^e	0.08	0.59
Methomyl	200 ^f	~1.8	~1.8
Methyl parathion	30 ^e	2.5	1.1
Molinate	20 ^d	8.9 ⁱ	96 ⁱ
Oxamyl	200 ^f	0.14	0.27
Parathion	30 ^d	0.25	1.83
Simazine	4 ^f /10 ^d	--	8.4
Thiobencarb	70 ^d /1 ^j	<1.0 ⁱ	4.9 ⁱ

^aAs referenced in California Department of Water Resources, Compilation of Federal and State Drinking Water Standards and Criteria, July 1993, or Association of Metropolitan Water Agencies Bulletin 94-3.

^bAs presented in reports and data reviewed for and referenced in this Technical Memorandum.

^cFMCL = Federal Maximum Contaminant Level.

^dSMCL = State Maximum Contaminant Level.

^eSAL = State action level.

^fPFMCL = Proposed Federal Maximum Contaminant Level.

^gData are unpublished. Concentrations are unknown but less than 200 µg/l.

^hRPHL = Recommended Public Health Level.

ⁱFrom 1987 through 1993.

^jSCLMCL = Secondary Maximum Contaminant Level established for taste and odor.

summer pesticide applications, and the first winter storm runoff. Monitoring was conducted on three agricultural drains, eight river/slough locations, and the five major export facilities intakes.

Over 2,400 analyses were conducted for 65 target pesticides and herbicides. In addition, samples were screened for pesticides detectable by mass spectrometry. Twenty-four of the 65 target pesticides and herbicides were detected a total of 94 times at or slightly above the detection level. All detected concentrations were below drinking water standards or California Department of Health Services (DHS) action levels (DWR, 1989).

DIDI. In 1988, DWR conducted the DIDI study to assess the impacts of Delta island agricultural drainage on the drinking water quality of Delta *source* water. The focus of the DIDI study was THMFP. A synoptic study was done as part of the DIDI, to characterize pesticide occurrence. The pesticide monitoring plan was based on the same evaluation of factors as the IDHAMP monitoring plan.

The monitoring was conducted on 30 Delta agricultural drains in July 1988. Pesticides were largely not detected. Six pesticides (atrazine, bentazon, carbaryl, methamidophos, molinate, and simazine) were detected in a few drains. All concentrations of detected pesticides were below drinking water standards *and/or* DHS action levels (DWR, 1990).

D-1485. DWR conducts monitoring for the *State Water Resources Control Board Water Rights Decision D-1485* Delta salinity requirements at 29 telemetered stations in the Delta. The furthest stations upstream are the Sacramento River at Greene's Landing and the San Joaquin River at Vernalis. The monitoring program consists primarily of electrical conductivity measurements. Limited sampling is also conducted for nutrients, metals, and various pesticides. A review of the pesticide data from 1990 through 1992 indicates that pesticides are rarely detected. Diuron was detected at a few locations in 1991.

Water Hyacinth Control Program. Since the early 1980s, the DBW has *attempted* to control water hyacinths in the Delta channels and sloughs through the direct application of 2,4-D.

The application of 2,4-D to control water hyacinths also occurs in the San Joaquin River system during the summer when there is insufficient flow to keep the waterways clear. In the San Joaquin River system, 2,4-D is applied to the San Joaquin River as far upstream as Merced County and *is also applied* to Salt Slough, the Merced River, and the Tuolumne River. At the request of the Regional Board, the DBW conducts periodic monitoring for 2,4-D, before, during, and after application. The DBW database is poorly organized; it is difficult to determine where the samples were collected and difficult to interpret the data. Concentrations of 2,4-D have not been detected above drinking water standards. Not infrequently, pre-application samples contain higher concentrations of 2,4-D (about 10 µg/l) than post-application samples (Personal Communication, Rudy Schnagl, Regional Board).

Delta Tributary Monitoring Programs

These studies, conducted in the Delta tributaries, focus primarily on ambient conditions with respect to biological resources rather than on drinking water quality. *The monitoring programs are summarized in Table 2 and detected pesticides with drinking water criteria are shown in Table 3.*

National Stream Quality Accounting Network. The United States Geological Survey (USGS) conducts routine water quality monitoring at various locations in the San Joaquin and Sacramento River systems. Routine water quality monitoring stations are the Sacramento River at Freeport, the Mokelumne River at Woodbridge, and the San Joaquin River at Vernalis. The overall focus of this USGS monitoring program is general chemistry. Of the three sites listed above, synoptic pesticides monitoring *has been conducted* only on the San Joaquin River at Vernalis.

Synoptic monitoring was conducted in the San Joaquin River at Vernalis in the fall of 1985 and again in 1988. In 1985, the USGS analyzed for 51 organic chemicals at Vernalis. Detection levels ranged from 1 to 3 µg/l. No pesticides were detected in the water samples. In the fall of 1988, the USGS analyzed for 35 organic chemicals at detection levels from 0.001 to

0.1 µg/l. Pesticides detected at or just above the detection level included cyanazine, DDE, DDT, diazinon, dieldrin, ethion, lindane, methyl parathion, metachlor, and parathion (USGS, 1985-1992).

In the fall of 1985, the USGS conducted synoptic pesticides monitoring of bed sediments and suspended sediments in the San Joaquin River system. The results of the study indicated DDD, DDE, DDT, and dieldrin are widespread in bed sediments of the San Joaquin River system. The highest concentrations occurred in the westside tributary streams, sloughs, and drains (Gilliom and Clifton, 1990).

The USGS is currently preparing a manuscript on DDT, its metabolites, and other pesticides, in water, suspended sediment, bed sediment, and the tissue of the Asian clam, Carbicula. Samples were collected in the San Joaquin basin at Orestimba Creek, Salt Slough, the Mokelumne River, the Stanislaus River, Dry Creek in Modesto, Turlock Irrigation District lateral canal number 5, and the San Joaquin River at Patterson and Vernalis. The USGS has sufficient data at some sites to establish a preliminary model of partitioning among the phases listed above. The manuscript is not yet available for review. (Personal Communication, Joe Domagalski, 1994).

San Joaquin River Bioassay Study. The Regional Board conducted periodic surveys from 1988 through 1990 for *aquatic* toxicity at various locations in the San Joaquin River system. The purpose of the study was to determine whether river *aquatic* toxicity occurred and if so, whether it was associated with agricultural practices. Repeated *aquatic* toxicity was found in the San Joaquin River between the confluence of the Merced and Stanislaus rivers. Detected pesticides included diazinon, methyl parathion, carbaryl, dimethoate, and carbofuran (Foe and Connor, 1991b). The two suspected sources were: (1) dormant spray pesticide application to orchards, and (2) pesticide application to alfalfa for weevil control.

San Francisco Bay Estuary Toxic Contaminants Program. This program is an umbrella program conducted by the USGS which has been examining pesticide input, transport,

and fate to the San Francisco Estuary. *Specific objectives are to: (1) determine how organic contaminants from riverine and local sources are transported and transformed under different hydrologic conditions, (2) determine ultimate fate of the organic contaminants within the Bay, and (3) detect or quantify ecological responses to the organic contaminants. Local sources include Delta farmlands, urban runoff, and petroleum refineries. The Sacramento and San Joaquin rivers are thought to contribute the greatest loads of pesticides to the estuary. (Kuivila and Nichols, date unknown).*

Monitoring has been conducted since 1990 on the Sacramento River at Sacramento and the San Joaquin River at Vernalis. Many of the state agency programs have been conducted in coordination with this program. Pesticide monitoring has focused on rice pesticides (molinate, thiobencarb, and carbofuran), orchard runoff (diazinon, methidathion, chlorpyrifos, and carbaryl), and alfalfa runoff (carbofuran and simazine). Currently, related data have been published by the state agency studies which have been conducted in coordination with the USGS program. (Personal Communication, Kathryn Kuivila, USGS). The USGS has published information on three monitoring studies conducted under this program: the Pesticide Tracer Study and Rice Pesticides Transport Study, both discussed later in this section, and a study conducted in 1991 in San Francisco Bay to examine the percent of pesticides in the dissolved form versus that sorbed onto suspended sediment.

The 1991 study included petroleum hydrocarbons, diazinon, and carbofuran. Carbofuran was detected only in solution. Ninety-eight percent of the total mass of diazinon was in solution. Further work is planned to investigate partition coefficients over a range of salinity for diazinon and chlorpyrifos (Domagalski and Kuivila, 1993).

San Joaquin River Study. The DPR, in collaboration with the Central Valley Regional Board, the USGS, and the California Department of Fish and Game (DFG) conducted a 2-year monitoring study at 18 sampling locations on both the major tributaries and the main stem of the San Joaquin River (from Stevenson to Vernalis). Monitoring was conducted from 1991 through 1993. Frequently detected pesticides were diazinon, methidathion, and chlorpyrifos in the winter,

carbofuran in the spring, and dimethoate and methomyl in the summer. Data from the study are partially published in a series of memoranda (Ross, 1991; 1992a; 1992b; 1993a; 1993b; 1993c). DPR is now evaluating best management practices (BMP) to reduce diazinon in orchard runoff. BMPs being evaluated involve cultural practices such as planting vegetative strips between orchard rows to increase soil permeability. (Personal Communication, Lisa Ross, DPR).

Winter Wheat Study. The DPR conducted a monitoring study for herbicides used on winter wheat crops in 1992. The study involved twice-weekly monitoring of the Colusa Basin Drain, Sutter Bypass, Feather River, and Sacramento River for 2,4-D, dicamba, and MCPA. All three herbicides were detected but at such low levels that no further study or mitigation was proposed. The data are not yet published. (Personal Communication, Pam Wofford, DPR).

Orchard and Alfalfa Study. In 1992, the Regional Board conducted a study of agricultural drainage from orchards and alfalfa crops. The purpose of the study was to determine (1) whether pesticides applied to orchards were causing toxicity in receiving waters (in the San Joaquin and Sacramento valleys), and (2) whether runoff from alfalfa fields causes toxicity in receiving waters. *The primary pesticides applied to orchards are parathion, diazinon, and chlorpyrifos. The primary pesticides applied to alfalfa are carbofuran, diazinon, malathion, diuron, chlorpyrifos, endosulfan, and trifluralin (Kuivila, 1991).*

The Orchard Study consisted of weekly monitoring of 11 sites in January and February 1992. Samples were collected during dry and wet weather. Six of the sites were small watercourses draining orchards. The other five sites were the Sacramento River above Colusa Basin Drain, the Feather River above the confluence with the Sacramento River, the Mokelumne River above the confluence with the Cosumnes River, the San Joaquin River at Bowman Road, and Old River. Thirty percent of the samples were toxic *to aquatic life*, primarily in the small watercourses. Samples collected during storm events were more toxic *to aquatic life* than those collected in dry weather. Pesticides detected in the samples *exhibiting aquatic toxicity* included diazinon, diuron, methidathion, bromacil, propham, and flumeturon.

The Alfalfa Study consisted of weekly monitoring of 13 sites in the Delta during March and April 1992. Samples were collected in dry weather only. Seven sites were small watercourses and six sites were in Delta sloughs. Thirteen percent of the samples were toxic to *aquatic life*. Pesticides detected in the samples *exhibiting aquatic toxicity* included: diazinon, diuron, chlorpyrifos, and carbofuran (Foe and Sheplaine, 1993).

National Water Quality Assessment Program. In 1991, the USGS initiated a water quality survey program of major river basins nationwide. The San Joaquin River was one of 20 river basins selected for study in 1991. The Sacramento River was one of 20 additional river basins selected for study in 1993. San Joaquin River monitoring was begun in 1992 and included general chemistry, nutrients, and pesticides. Monitoring in the Sacramento River Basin has not yet begun.

Monitoring for pesticides in the San Joaquin River Basin was conducted in Orestimba Creek, the Merced River, and the San Joaquin River at Vernalis. The sampling period was April through September 1992 and December 1992 through February 1994. Monitoring frequency varied between three times a week to once a month, depending on the sampling location and the season. A preceding literature review led to a pesticide sampling scheme based on winter, spring, and summer pesticide usage. The surface water pesticide monitoring is complete and the study will next address the relationship between pesticides, crop types (grapes and almonds), and groundwater contamination. Frequently detected *insecticides* included diazinon (in the winter and summer) and chlorpyrifos and methidathion in the spring. Frequently detected herbicides included simazine, triazine, and metolachlor. These data *will be published in a Retrospective Report for the San Joaquin Basin National Water Quality Assessment Program*. (Personal Communication, Joe Domagalski, USGS).

Pesticide Tracer Study. The USGS conducted a tracer study of pesticide transport from the Sacramento and San Joaquin River systems through the Delta. The study was conducted in cooperation with the Regional Board as part of the San Francisco Bay-Estuary Toxic Contaminants Study. The purpose was to characterize orchard dormant pesticide spray fate and

transport. The monitoring plan was designed to catch storm runoff events following the annual winter dormant pesticide spray applications to orchards. Dormant pesticide sprays were applied to many Central Valley orchards during two weeks of dry weather in January 1993. Storm events in early February 1993 were then monitored. The monitoring was specifically designed to follow storm discharges through the Sacramento and San Joaquin River systems. Monitoring locations were the Sacramento River at Sacramento, Rio Vista, and Chipps Island; the San Joaquin River at Vernalis and Stockton; and the Carquinez Straight at Martinez.

Dissolved diazinon in storm runoff moved through the river systems (with a time lag of one to three days following storm events) until mixed and dissipated by sea water in San Francisco Bay. The maximum concentration detected was 1,070 ng/l in the San Joaquin River at Vernalis. The Regional Board conducted *aquatic toxicity tests* on the sample water. River samples before and after the storm transport of diazinon were not toxic *to aquatic life*. During the storm runoff transport, the river water produced 100 percent mortality. Other analyses on the storm runoff river water showed the presence of additional pesticides: chlorpyrifos, methidathion, and carbaryl (Kuivila, 1993).

Rice Field Drainage. Water quality monitoring and toxicity testing in rice field agricultural drains conducted as part of the State's interagency Rice Pesticide Control Program are discussed in this section. *The primary pesticides applied to rice are carbofuran, methyl parathion, molinate, and thiobencarb (Kuivila, 1991).* There is also a discussion of how these and other studies have resulted in performance goals and management practices for five pesticides found in rice drainage. *There have been two driving forces in managing pesticides in rice field drainage. The first was the issue of seasonal taste and odor problems during the spring in the City of Sacramento's treated Sacramento River water in the 1980s. These taste and odor problems were attributed to thiobencarb concentrations from rice field drainage. The highly successful management practices instituted by rice growers in the 1980s have resulted in eliminating thiobencarb taste and odor problems in Sacramento River water. The second driving force in rice field drainage is the effect of rice pesticides on aquatic life. This issue is continuing to be studied and addressed. It should be noted that studying and controlling pesticides in rice*

field drainage has produced a larger body of data than for any other pesticide source in the Central Valley.

Rice Field Drainage Pesticide Chemistry Monitoring. Pesticide monitoring has been conducted in rice growing area agricultural drains (principally Colusa Basin Drain, Butte Slough, and Sacramento Slough) and in the Sacramento River near Sacramento by the DFG since 1980 (Finlayson, et al; 1982, 1983, 1984, 1985, 1986, 1991, 1993; Harrington and Lew, 1988; DPR, 1984-1993). Results for each pesticide are summarized below.

Molinate (Ordram). The peak concentration of molinate in an agricultural drain was measured at 697 µg/l in 1981. A steady reduction in concentrations occurred between 1981 and 1986. From 1987 through 1993, peak concentrations have ranged between 6.2 and 96 µg/l. In the Sacramento River, the peak concentration of molinate was measured at 27 µg/l in 1982. The reduction in agricultural drainage concentrations, *in addition to other factors (such as water conservation efforts and development of recirculating systems)*, has resulted in a corresponding reduction in river concentrations between 1982 and 1986. From 1987 through 1993 peak concentrations in the river have ranged from *nondetectable (detection limit 1.0 µg/l)* to 8.9 µg/l.

Thiobencarb (Bolero). The peak concentration of thiobencarb in an agricultural drain was measured at 170 µg/l in 1982. A steady reduction in concentrations occurred between 1982 and 1986. From 1987 through 1993, peak concentrations have ranged between *nondetectable (detection limit 1.0 µg/l)* and 4.9 µg/l. In the Sacramento River, the peak concentration of thiobencarb was measured at 6 µg/l in 1982. From 1987 through 1993, the concentration in the river has been *nondetectable (detection limit 1.0 µg/l)*.

Carbofuran (Furadan). This pesticide was monitored in agricultural drains between 1988 and 1993 with concentrations ranging from *nondetectable (detection limit 1.0 µg/l)* to 4.4 µg/l. In 119 samples collected from the Sacramento River during this time period, carbofuran has been detected three times. The peak concentration in the river was measured at 0.6 µg/l.

Bensulfuron methyl (Londax). This pesticide was monitored in agricultural drains from 1989 through 1993. Detected concentrations have been highly variable, ranging from *nondetectable (detection limit 0.5 µg/l)* to 2.10 µg/l. In 27 samples collected from the Sacramento River during this time period, bensulfuron methyl was not detected (detection limit 0.5 µg/l).

Malathion. This pesticide was monitored between 1990 and 1993 in agricultural drains. The measured concentrations are mostly *nondetectable (detection limit 0.10 µg/l)*. The peak concentration measured was 0.59 µg/l. In 43 samples collected from the Sacramento River during this time period, malathion was not detected (detection level 0.10 µg/l).

Methyl parathion. This pesticide was monitored between 1990 and 1993 in agricultural drains. The measured concentrations are mostly *nondetectable (detection limit 0.10 µg/l)*. The peak concentration measured was 1.1 µg/l. In 43 samples collected from the Sacramento River during this time period, methyl parathion was not detected (detection limit 0.10 µg/l).

Propanil. This pesticide was monitored in an agricultural drain in 1987 and 1988. The pesticide was detected *twice* in 28 samples, at a concentration of 1.6 µg/l. All other samples were *nondetectable (detection limit 0.5 µg/l)*. In 28 samples collected from the Sacramento River during this period, propanil was not detected (detection limit 0.5 µg/l).

Carbaryl. This pesticide was monitored three times in an agricultural drain in 1987 and 1988. It was not detected at a detection limit of 0.1 µg/l. Carbaryl was not detected in the *six* samples collected from the Sacramento River during this time period (detection limit 0.1 µg/l).

Rice Field Drainage Toxicity Testing. The Regional Board and DFG conducted *aquatic* toxicity testing in several rice field drains from 1986 through 1989. This work was part of an overall *aquatic* toxicity assessment of the Sacramento River. Toxicity was known to occur in the river upstream of the rice cultivation area (attributed to mine drainage). The goal of this

study was to determine whether rice drainage also contributed to toxicity in the Sacramento River.

Aquatic toxicity testing was conducted in May and June during the initial release of herbicide treated water from rice fields and also at several other times of year. The testing occurred in Colusa Basin Drain, Butte Slough, and Sacramento Slough, three of the principal rice area agricultural drains. The study concluded that rice drainage *was* frequently toxic to aquatic life during May and June. The *rice field* drainage was generally not toxic during other times of the year. Pesticides detected in samples *exhibiting aquatic toxicity* were:

- 1986 - methyl parathion, chlorpyrifos
- 1987 - methyl parathion, carbofuran, malathion
- 1988 - methyl parathion, carbofuran
- 1989 - methyl parathion, carbofuran, malathion

Aquatic toxicity during May and June was also found in the Sacramento River as far downstream of the rice fields as Rio Vista.

Additional *aquatic* toxicity testing was conducted by the DFG and the Regional Board in April through June of 1990. *Aquatic* toxicity testing and chemistry monitoring were conducted three times a week on Colusa Basin Drain. This work identified the specific toxicant as methyl parathion. This work resulted in proposed changes in management practices for the use of methyl parathion on rice fields (Foe and Connor, 1991a).

Rice Pesticides Transport Study. In June 1990, the USGS monitored a "parcel" of water moving through the Sacramento River system from below Colusa Basin Drain to Rio Vista. The parcel was sampled every 6 hours for molinate, thiobencarb, carbofuran, and methyl parathion. The results indicated a slight decreasing trend in molinate concentrations from upstream to downstream but no recognizable decrease in thiobencarb or carbofuran concentrations. Methyl

parathion degradation products were detected in the parcel, but not methyl parathion (Domagalski and Kuivila, 1991).

Other Studies, Performance Goals, and Management Practices. The DPR conducted a study in *May* 1991 to determine whether drift from aerial spraying is a significant factor in methyl parathion concentrations in rice field drainage water. Methyl parathion is applied to control tadpole shrimp. Four agricultural drainage ditches in Colusa County were sampled before and after aerial spraying. The results suggested that methyl parathion levels may increase when the flight path parallels the drainage ditch (Pino, et al, 1992). *Future evaluation of this issue will involve the examination of the potential contribution of seepage through levees to pesticide contamination in the canals.*

The DFG is in the process of conducting a hazard assessment of various pesticides with respect to their effects on aquatic life. The proposed use of the hazard assessment will be to provide the Regional Board with criteria for pesticides, *based on DFG's latest review* of the impact of pesticides on the aquatic habitat. These criteria are considered *by the Regional Board when setting Performance Goals and water quality objectives* (Personal Communication, Rudy Schnagl, 1994).

The DPR began their rice herbicide control program in 1983 - focused primarily on molinate and thiobencarb. In 1990, the Regional Board adopted a Basin Plan Amendment which set performance goals for five pesticides in agricultural drainage. *The management practices that will be followed to meet the performance goals are reviewed annually.* The 1993 performance goals are:

Carbofuran	0.4 µg/l
Malathion	0.1 µg/l
Methyl parathion	0.13 µg/l
Molinate	10 µg/l
Thiobencarb	1.5 µg/l

The discharge of agricultural drainage containing these pesticides is prohibited unless the discharger is following appropriate management practices. Rice field agricultural drainage water quality has moved closer to, but often does not meet, these performance goals. Factors that affect the concentrations include weather (pesticides dissipate more quickly under warmer temperatures), drought conditions (although there is less available dilution, there is also generally less discharge and less total mass of pesticides discharged), and emergency releases (releases made to protect crops before holding times are completed).

The *appropriate* management practice for *all* pesticides listed above involves retaining the treated water on the field for varying degrees of time. *Soil incorporation of carbofuran is also being investigated as an appropriate management practice (Nicosia, Carr, Gonzales, and Orr, 1991).* Management practices that were added for the 1993 growing season include a 100-foot buffer zone next to canals on the downwind side of *methyl parathion* aerial applications and actively discouraging emergency releases. These management practice programs are implemented through the county Agricultural Commissioners (Lee and Gorder, 1993).

There is a Memorandum of Understanding between the *State* Board and the DPR to coordinate their efforts on pesticides registration, studies, and monitoring efforts. Currently, a Management Agency Agreement is being *developed* which would *facilitate Regional Board recommendations on the selection and prioritization of pesticides to be monitored and give more detail on how pesticide control efforts will be conducted to protect water quality.* (Personal Communication, Rudy Schnagl, 1994).

Review of Nine Pesticides. In 1993, the Regional Board assembled information on nine pesticides detected in Central Valley surface waters which Regional Board staff believe contribute to aquatic toxicity. The information is summarized in Table 4 (Sheipline, 1993).

Four Rivers Project. The DPR and DFG are initiating a year-long pesticide monitoring program on four California rivers. The Sacramento and Merced rivers are in the Delta watershed. The other rivers are the Russian and Salinas rivers. The monitoring will consist of weekly

Table 4. Pesticides Which May Contribute to Aquatic Toxicity in Central Valley Surface Waters

Chemical name	Trademark name	Type of pesticide	Range of concentration detected in Central Valley surface waters, µg/l	Criteria, µg/l	Persistence in surface waters	Usage	Months used	Counties with highest total application
Carbaryl	Sevin	Carbamate insecticide	0.6 to 8.4	0.02 ^a	1.3 to 5.8 days	Row crops Orchards Landscapes	January through December	Tulare Kern Fresno
Methomyl	Lannate	Carbamate insecticide	0.06 to 5.4	None	Unknown	Row crops Field crops Citrus orchards	March through October	Fresno Kern Tulare
Oxamyl	Vydate	Carbamate insecticide	0.12 to 0.14	None	Unknown	Row crops Orchards	May through August	San Joaquin Merced Stanislaus
Chlorpyrifos	Dursban Lorsban	Organophosphate insecticide	0.01 to 1.6	0.041 ^b	7.1 to 53 days	Orchards Row crops Field crops Landscapes Structures	January through December	Tulare Fresno Kern
Diazinon	Basudin Diazitol	Organophosphate insecticide	0.02 to 6.84	0.009 ^a	12 hours to 6 months	Orchards Row crops Field crops Landscapes Structures	January through December	Fresno Kern Merced
Dimethoate	Cygon Perfekthion Roxion Fostion Rogor	Organophosphate insecticide	0.05 to 1.05	None	8 weeks	Orchards Row crops Field crops	May through August	Tulare Kern Fresno
Fonofos	Dyfonate	Organophosphate insecticide	0.01 to 0.54	None	12 to 127 days	Row crops	April	San Joaquin Sacramento Stanislaus
Methidathion	Supracide Ultracide	Organophosphate insecticide	0.14 to 15.1	None	Unknown	Orchards Field crops	November through September	Tulare Fresno Kings Kern
Diuron	Karmex	Urea herbicide	0.1 to 30.6	1.6 ^a	Unknown	Orchards Field crops Landscape	January through December	Tulare Fresno Kern San Joaquin

Source: Sheipline, Robert. Background Information on Nine Selected Pesticides. California Regional Water Quality Control Board, Central Valley Region. Draft Staff Report. September 1993.

^aNational Academy of Sciences recommended maximum in surface waters.

^bEPA 4-day freshwater criteria.

pesticide chemistry testing and *aquatic* toxicity testing every two weeks. Sacramento River monitoring (at Sacramento) began in the fall of 1993. Monitoring on the Merced River *began June 1994. Monitoring on the Russian and Salinas rivers began August 1994.* No data are published or available. (Personal Communication, Robert Fujimura, DFG).

Bay-Delta Oversight Council Toxic Substances Study. *The Bay-Delta Oversight Council (BDOC) has commissioned staff at the University of California at Davis to conduct a study of the effects of toxic substances in fish, wildlife, and plant resources of the Bay-Delta estuary. The study will consist of a summary and evaluation of existing literature with respect to trace elements, pesticides, and other organic compounds. Sources; geographical distribution; effect on fish, wildlife, and plants; and an assessment of control and monitoring programs will be described. The study is expected to be completed by the end of 1994.*

Sacramento Ambient Monitoring Program. The City of Sacramento, the Sacramento County Water Agency, and the Sacramento Regional County Sanitation District began biweekly ambient monitoring in the American and Sacramento rivers in 1993. In 1994, organophosphorus pesticide monitoring will be added to the list of constituents sampled. The City and County of Sacramento are Co-permittees in a National Pollutant Discharge Elimination System (NPDES) Stormwater Permit. The impetus for this additional analysis is the concern, based on recent Regional Board work, that urban stormwater runoff may be contributing pesticides to receiving waters in concentrations toxic to aquatic life.

Sacramento Urban Runoff Toxicity Studies. The Regional Board and the Sacramento Stormwater NPDES Permittees are conducting studies to determine the chemicals responsible for aquatic toxicity in urban runoff. Toxicity testing was conducted during two storm events in 1993 and one storm event in 1994 in a total of 21 Sacramento and Stockton urban runoff discharges and urban creeks and sloughs. *Aquatic* toxicity was seen in all urban runoff discharge samples and most urban creeks and sloughs. The results indicate that organophosphorus pesticides are the likely toxicants and that diazinon is the primary toxicant. The highest concentration of diazinon measured was 1.1 µg/l. Additional toxicants appear to be present but have not yet been

identified (Connor, 1994). The study will likely continue during the 1994/1995 rain season. The Regional Board is currently conducting a survey on diazinon in dry weather urban runoff.

The Regional Board is proposing to conduct a study on diazinon occurrence in atmospheric dry deposition and rainfall. The Bay Area Regional Board is proposing to conduct a study to identify the most significant diazinon sources in urban watersheds and develop corresponding source control measures (Personal Communication, Valerie Connor, 1994).

Pesticide Issues Regarding Water Treatment Plant Operations

Recently, the use of copper sulfate for algal control and chlorine for disinfection by water treatment plants has arisen as a pesticide usage and control issue which may be regulated by county Agricultural Commissioners. The Inyo-Mono Counties Agricultural Commissioner is requiring water treatment plants to obtain a Pesticide Operations Identification number and submit monthly summary pesticide reports. Regulation of these chemicals as pesticides at the water treatment plant is not, per se, the focus of this technical memorandum. However, the information is relayed herein as it relates generally to the pesticides topic.

OVERALL FINDINGS RELEVANT TO THIS STUDY

This section discusses the pesticide data collected in the Delta and Delta tributary watersheds with respect to (1) its effect on the drinking water quality of the Delta and the Delta tributaries *source water*, (2) its relevance with regard to loads calculations for this study, and (3) an assessment of the need for additional pesticide monitoring.

Pesticides with significant agricultural or urban applications in the Delta tributary watersheds are detected in the river system. No pesticides have been detected in the rivers at concentrations above drinking water standards. With the exceptions of occasional molinate

concentrations in rice field drainage and diazinon concentrations in San Joaquin River westside drains, no pesticide has been detected in a drain at concentrations above drinking water standards. *The decline in molinate (and thiobencarb) in the Sacramento River over the past 10 years has illustrated the potential of agricultural best management practices in improving agricultural drainage water quality and its effect on the water quality of receiving waters. Molinate has been reduced from an estimated 18,000 pounds transported in the Sacramento River in 1982 to 2,000 pounds in 1993. Thiobencarb has been reduced from a high of over 2,000 pounds in 1985 to 51 pounds in 1990.* In general, pesticide concentrations are at least an order of magnitude lower than drinking water standards. These concentrations, are, *however*, of considerable concern to aquatic life and are considered responsible for some of the *aquatic* toxicity found in Delta tributary rivers.

Again, it should be noted that this technical memorandum has summarized pesticide monitoring data in sources of drinking water rather than in drinking water itself. Water treatment processes remove contaminants from source waters. Water utilities are, however, concerned with the presence of pesticides in source water for several reasons. First, some pesticides are detected for which there are no drinking water standards. For these pesticides, it is less clear that the concentrations in source waters are too low to adversely affect human health. Second, although individual pesticides are detected well below drinking water standards, the possible synergistic effects of several pesticides present in sources of drinking water are not well known. Third, there is a public perception that pesticides should not be present in sources of drinking water, regardless of the concentrations. Finally, water supplies taken from the Delta and Delta tributaries are in jeopardy, particularly during dry years, due to the decline in the ecological resources of the Bay/Delta system. Pesticides are of considerable concern to aquatic resources and may be partially responsible for the decreased populations of fish and other aquatic organisms. Because aquatic resources are driving water management of the Bay-Delta and its tributaries, all potential causes of negative impacts on the aquatic community are of concern to drinking water utilities.

Pesticides are not recommended for inclusion in the calculations of loads for this study. Although there has been considerable pesticide monitoring conducted, it appears that pesticide concentrations are extremely episodic due both to "pesticide seasons" based on agricultural crop practices and the timing of the application relative to storm events. The calculation of mass loads based on grab samples, therefore, may be particularly nonrepresentative. In addition, there are more significant constituents (relative to drinking water) for inclusion in the calculation of mass loads. With respect to the study of various control alternatives, however, it seems apparent that effective control of agricultural (and to a less extent, urban runoff) discharges would reduce the loads of pesticides into the Delta tributaries. *Control of pesticides in agricultural and urban runoff discharges is proceeding due to impacts to aquatic resources. Controlling pesticide concentrations to reduce and/or eliminate impacts on aquatic life will most likely result in levels well below either human health or taste and odor drinking water quality concerns. The Phase II/V compound monitoring (discussed below) may or may not change this assessment. California Urban Water Agencies (CUWA) members support appropriate efforts to control pesticides in discharges to Delta tributaries as benefitting the Delta as a source of drinking water.*

The work currently being done by various state and federal agencies to manage pesticides with respect to their impact on aquatic resources is likely to keep pesticide levels in the Delta tributary source waters well below drinking water standards. Therefore, no additional pesticide monitoring is recommended for this study. In addition, there are two major upcoming areas of monitoring which will provide additional pesticide data for future evaluation regarding pesticides in drinking water. The first is the continuing work being done by the USGS and various state agencies (Regional Board, DPR, and DFG) regarding the identification and control of pesticides which affect aquatic life. The second is the upcoming work that water utilities will need to conduct to comply with the Phase II/V Regulations. This will involve some combination of a "vulnerability assessment," which looks in more detail at specific regulated organic chemical usage in a water utility's watershed, and/or monitoring at the utility's intake.

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